A comprehensive probabilistic model of chloride ingress in unsaturated concrete

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Abstract

Corrosion induced by chloride ions becomes a critical issue for many reinforced concrete structures. The chloride ingress into concrete has been usually simplified as a diffusion problem where the chloride concentration throughout concrete is estimated analytically. However, this simplified approach has several limitations. For instance, it does not consider chloride ingress by convection which is essential to model chloride penetration in unsaturated conditions as spray and tidal areas. This paper presents a comprehensive model of chloride penetration where the governing equations are solved by coupling finite element and finite difference methods. The uncertainties related to the problem are also considered by using random variables to represent the model parameters and the material properties, and stochastic processes to model environmental actions. Furthermore, this approach accounts for: (1) chloride binding capacity; (2) time-variant nature of temperature, humidity and surface chloride concentration; (3) concrete aging; and (4) chloride flow in unsaturated conditions. The proposed approach is illustrated by a numerical example where the factors controlling chloride ingress and the effect of weather conditions were studied. The results stress the importance of including the influence of the random nature of environmental actions, chloride binding, convection and two-dimensional chloride ingress for a comprehensive lifetime assessment.

Key words:
Chloride ingress, corrosion, reinforced concrete, reliability, finite element method

1. Introduction

Corrosion of steel reinforcement becomes a critical issue for many reinforced concrete (RC) structures, in particular, when they are located in chloride-contaminated environments and/or exposed to carbon dioxide. Given the high alkalinity of concrete at the end of construction, a thin passive layer of corrosion products protects steel bars against corrosion, and therefore, the structure is insusceptible to corrosion attack. However, chloride-induced corrosion begins when the concentration of chlorides at the steel bars reaches a threshold value destroying the protective layer. The mechanisms by which corrosion affects load carrying ca-

pacity of RC structures are: loss of reinforcement section, loss of steel-concrete bond, concrete cracking and delamination. Therefore, design or retrofitting of structures susceptible to corrosion should ensure optimum levels of operationally and safety during their life-cycle.

Since chloride penetration into concrete matrix is paramount to corrosion initiation, several studies have been focused on understanding and modeling the phenomenon. Chloride ingress implies a complex interaction between physical and chemical processes. However, under various assumptions, this phenomenon can be simplified to a diffusion problem [1]. The analytical solution of the diffusion equations based on the error function is valid only when RC structures are saturated and subject to constant concentration of chlorides on their exposed surfaces. Nevertheless, these conditions are only valid for submerged zones where the low concentration of dissolved oxygen reduces considerably corrosion risks in comparison to unsaturated zones. There are other analytical solutions to the Fick's second law based on the Mejlbro function [2]. This approach, called Mejlbro-Poulsen or HETEK model, solves the most part of the shortcoming of the solutions based on the error functions. For instance, it considers the time-dependency of the apparent diffusion coefficient as well as the chloride concentration of the exposed surface. Besides, the HETEK model also provides the model parameters for a wide range of concrete compositions and environmental conditions obtained from experimental tests. This model also proposes a numerical solution to account for chloride ingress by convection and the effect of chloride binding. However, the interaction between chloride penetration and temperature and chloride ingress in two dimensions are not considered by the HETEK model. Besides, the analytical approach does not consider chloride binding and concrete aging. Other researches have directed their efforts to enhance the chloride ingress modeling in saturated and unsaturated conditions. Saetta et al. [3] and Ababneh et al. [4] proposed various models to account for the dependence on environmental conditions and concrete mix parameters for chloride ingress in unsaturated concrete. These models solved the nonlinear and coupled partial differential equations by coupling finite element and finite difference methods.

A comprehensive model of chloride ingress should also consider the uncertainties related to the phenomenon to make rational predictions of the lifetime of structures. There are three sources of uncertainties in this problem. The first one is related to the randomness of material properties, the second one encompasses the uncertainties in the model and their parameters, and the third one is concerned with the random nature of environmental actions. Therefore, lifetime assessment of deteriorating RC structures should be based on probabilistic methods and a comprehensive model of the coupled effect of various deterioration processes (e.g., corrosion, fatigue, creep, etc.) [5, 6, 7]. Among the works concerning probabilistic modeling of chloride penetration, it is important to highlight the study carried out by Kong et al. [8]. This study is based on the model of Ababneh et al. [4] and performs a reliability analysis that takes into consideration the uncertainties of material properties. However, this approach only studied the case of saturated concrete. More recently, Val and Trapper [9] considered the model presented in [3, 10] to perform a probabilistic eval-

uation of corrosion initiation time. Such work focused mainly on the influence of one- and two-dimensional flow of chlorides on the assessment of the probability to corrosion initiation. Nevertheless, it does not consider heat flow into concrete and the impact of the stochastic nature of humidity, temperature and chloride concentration in the concrete surface.

Within this context, this paper presents a probabilistic approach to RC deterioration that takes into consideration the uncertainty of chloride ingress, particularly, the uncertainty related with environmental actions. Based on the works by Saetta et al. and Martín-Pérez et al. [3, 10], the proposed methodology solves the governing equations of chloride ingress in unsaturated concrete by using a numerical approach which combines the finite element method with a finite difference scheme. This approach accounts mainly for:

- chloride binding capacity of the cementitious system,
- time-variant nature and the effects of temperature, humidity and chloride concentration in the surrounding environment,
- decrease of chloride diffusivity with concrete age and
- one- and two-dimensional flow of chlorides in unsaturated concrete.

The originality of the present work lies in the realistic (stochastic) modeling of environment actions (temperature, humidity and surface chloride concentration) coupled with a realistic model of chloride ingress for unsaturated concrete structures. Nevertheless, this study does not consider the effect of concrete cracking that can increase concrete diffusivity [2, 11]. Section 2 depicts the governing equations of the model of chloride ingress. Their solution and a deterministic example are presented in section 3. Section 4 introduces the proposed stochastic approach which is illustrated in section 5.

2. Chloride ingress in unsaturated concrete

The ingress of chloride ions into concrete is defined by a complex interaction between physical and chemical processes, which has been usually treated as a diffusion problem modeled by Fick's second law. Many deterministic and probabilistic studies adopt a simplified solution to Fick's law where the chloride concentration at a given time and position, $C(x,t)$, is estimated by an error function $erf(\cdot)$ [1]:

$$C(x,t) = C_{env}\left[1 - erf\left(\frac{x}{2\sqrt{D_c t}}\right)\right] \tag{1}$$

where C_{env} is the surface chloride concentration, D_c is the chloride diffusion coefficient, t is the time and x is the depth in the diffusion direction. Such a solution is valid when the material is homogeneous, the diffusion coefficient is constant in time and space, the material is saturated and the concentration in the concrete

surface remains constant during the exposure. Naturally, these conditions are never satisfied. Concrete is a heterogeneous material that is frequently exposed to time-variant surface chloride concentrations. In addition, given the high corrosion rates presented in unsaturated conditions, modeling chloride ingress for structures subject to drying-wetting cycles becomes a critical issue. Saetta et al. [3] and latter Martín-Pérez et al. [10] presented an alternative solution to Fick's law to enhance the chloride ingress prediction. This section presents the governing equations of the problem which consider the interaction between three phenomena:

1. chloride transport;
2. moisture transport; and
3. heat transfer.

Each phenomenon is represented by a partial differential equation (PDE) and their interaction is considered by solving simultaneously the system of PDEs. The following subsections present each phenomenon separately and section 3 summarizes the numerical procedure to solve the whole PDE system.

2.1. Chloride transport

Frequently, diffusion is considered the main transport process of chlorides into concrete. However, for partially-saturated structures, chloride ingress by capillary sorption or convection becomes an important mechanism. The chloride ingress process is a combination of diffusion and convection. Diffusion denotes the net motion of a substance from an area of high concentration to an area of low concentration. Convection refers to the movement of molecules (e.g., chlorides) within fluids (e.g., water). To account for both mechanisms in the assessment of chloride ingress, a convective term is added to Fick's second law of diffusion [10]:

$$\frac{\partial C_{tc}}{\partial t} = \underbrace{\text{div}\left(D_c w_e \overrightarrow{\nabla}\left(C_{fc}\right)\right)}_{\text{diffusion}} + \underbrace{\text{div}\left(D_h w_e C_{fc} \overrightarrow{\nabla}\left(h\right)\right)}_{\text{convection}} \tag{2}$$

where C_{tc} is the total chloride concentration, t is the time, D_c is effective chloride diffusion coefficient, w_e is the evaporable water content, C_{fc} is the concentration of chlorides dissolved in the pore solution –i.e., free chlorides, D_h is the effective humidity diffusion coefficient and h is the relative humidity. Equation 2 represents the change of the total chloride concentration, C_{tc}, as a function of the spatial gradient of free chlorides, C_{fc}. During chloride transport into concrete, chloride ions are present in the following states: (1) dissolved in the pore solution (free chlorides), (2) chemically bound to the hydration products of cement, or (3) physically sorbed on the surfaces of the gel pores [12]. If the concentrations of chemically bound and physically sorbed chlorides are grouped in the concentration of bound chlorides, C_{bc}, the total chloride concentration is:

$$C_{tc} = C_{bc} + w_e C_{fc} \tag{3}$$

Thus, Equation 2 can be rewritten in terms of the concentration of free chlorides. For instance, for a bidimensional flow of chlorides in x and y directions Equation 2 becomes:

$$\frac{\partial C_{fc}}{\partial t} = D_c^* \left(\frac{\partial^2 C_{fc}}{\partial x^2} + \frac{\partial^2 C_{fc}}{\partial y^2} \right) + D_h^* \left[\frac{\partial}{\partial x} \left(C_{fc} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(C_{fc} \frac{\partial h}{\partial y} \right) \right] \tag{4}$$

where D_c^* and D_h^* represent the apparent chloride and humidity diffusion coefficients, respectively:

$$D_c^* = \frac{D_c}{1 + (1/w_e)\,(\partial C_{bc}/\partial C_{fc})} \tag{5}$$

$$D_h^* = \frac{D_h}{1 + (1/w_e)\,(\partial C_{bc}/\partial C_{fc})} \tag{6}$$

where $\partial C_{bc}/\partial C_{fc}$ is the binding capacity of the cementitious system which is given by the slope of a binding isotherm [13]. The binding isotherm relates the free and bound chloride concentrations at equilibrium and is characteristic of each cementitious system. The isotherms mostly used to estimate the binding capacity are [14, 15]: (1) Langmuir isotherm:

$$C_{bc}^L = \frac{\alpha_L C_{fc}}{1 + \beta_L C_{fc}} \tag{7}$$

and (2) Freundlich isotherm:

$$C_{bc}^F = \alpha_F C_{fc}^{\beta_F} \tag{8}$$

where α_L, β_L, α_F and β_F are binding constants obtained empirically from regression analyses. The content of tricalcium aluminate C_3A affects substantially the binding capacity of cement. Therefore, isotherms are comparable only when their constants are defined for the same content of C_3A. On the other hand, experimental evidence has shown that the effective chloride diffusion coefficient depends mainly on temperature, pore relative humidity, concrete aging, cement type, porosity and curing conditions [3]. The effects of temperature, humidity and concrete aging can be estimated by correcting a reference diffusion coefficient, $D_{c,ref}$, which has been measured at standard conditions [3, 10]:

$$D_c = D_{c,ref}\ \ f_1(T)\, f_2(t)\, f_3(h) \tag{9}$$

where $f_1(T)$, $f_2(t)$ and $f_3(h)$ are correction expressions for temperature, aging and humidity, respectively. Namely:

$$f_1(T) = \exp\left[\frac{U_c}{R} \left(\frac{1}{T_{ref}} - \frac{1}{T} \right) \right] \tag{10}$$

where U_c is the activation energy of the chloride diffusion process in kJ/mol, R is the gas constant ($R = 8.314$ J/(mol °K)), T_{ref} is the reference temperature at which the reference diffusion coefficient, $D_{c,ref}$, has been evaluated ($T_{ref} = 276$ °K) and T is the actual absolute temperature inside concrete in °K.

$$f_2(t) = \left(\frac{t_{ref}}{t} \right)^m \tag{11}$$

where t_{ref} is the time of exposure at which $D_{c,ref}$ has been evaluated ($t_{ref} = 28$ days), t is the actual time of exposure in days and m is the age reduction factor.

$$f_3(h) = \left[1 + \frac{(1-h)^4}{(1-h_c)^4}\right]^{-1} \tag{12}$$

where h is the actual pore relative humidity and h_c is the humidity at which D_c drops halfway between its maximum and minimum values. Bažant and Najjar reported that h_c remains constant for different concretes or cement pastes –i.e., $h_c = 0.75$ [16].

2.2. Moisture transport

Moisture flow in concrete also follows Fick's law and can be expressed in terms of the pore relative humidity, h, as follows [17]:

$$\frac{\partial w_e}{\partial t} = \frac{\partial w_e}{\partial h}\frac{\partial h}{\partial t} = \text{div}\left(D_h \overrightarrow{\nabla}(h)\right) \tag{13}$$

As for chloride diffusion, the humidity diffusion coefficient depends on many factors and can be estimated in terms of a reference humidity diffusion coefficient, $D_{h,ref}$:

$$D_h = D_{h,ref} \;\; g_1(h)\, g_2(T)\, g_3(t_e) \tag{14}$$

The function $g_1(h)$ takes into consideration the dependence on pore relative humidity of concrete:

$$g_1(h) = \alpha_0 + \frac{1-\alpha_0}{1 + [(1-h)/(1-h_c)]^n} \tag{15}$$

where α_0 is a parameter that represents the ratio of $D_{h,min}/D_{h,max}$, h_c is the value of pore relative humidity at which D_h drops halfway between its maximum and minimum values ($h_c = 0.75$ [16]) and n is a parameter that characterizes the spread of the drop in D_h. The function $g_2(T)$ accounts for the influence of temperature on D_h:

$$g_2(T) = \exp\left[\frac{U}{R}\left(\frac{1}{T_{ref}} - \frac{1}{T}\right)\right] \tag{16}$$

where U is the activation energy of the moisture diffusion process in kJ/mol and T_{ref} is the reference temperature at which $D_{h,ref}$ was measured ($T_{ref} = 276$ °K). Finally, $g_3(t_e)$, considers the dependency on the degree of hydration attained in concrete:

$$g_3(t_e) = 0.3 + \sqrt{\frac{13}{t_e}} \tag{17}$$

where t_e represents the hydration period in days. To solve Equation 13, it is also necessary to determinate the moisture capacity $\partial w_e/\partial h$. For a constant temperature, the amount of free water, w_e, and pore relative

humidity, h, are related by adsorption isotherms. According to the Brunauer-Skalny-Bodor (BSB) model, the adsorption isotherm can be estimated as [18]:

$$w_e = \frac{CkV_m h}{(1-kh)\left[1+(C-1)\,kh\right]} \tag{18}$$

where C, k and V_m are parameters depending on temperature, water/cement ratio, w/c, and the degree of hydration attained in the concrete. Xi et al. [19] developed experimental expressions for such parameters; for instance, for $t_e \geq 5$ days and $0.3 < w/c \leq 0.7$:

$$C = \exp\left(\frac{855}{T}\right) \tag{19}$$

$$k = \frac{(1-1/n_w)\,C-1}{C-1} \tag{20}$$

$$n_w = \left(2.5+\frac{15}{t_e}\right)(0.33+2.2w/c)\,N_{ct} \tag{21}$$

$$V_m = \left(0.068-\frac{0.22}{t_e}\right)(0.85+0.45w/c)\,V_{ct} \tag{22}$$

where N_{ct} and V_{ct} depend on the type of cement; e.g. for the type II Portland cement $N_{ct} = V_{ct} = 1$.

2.3. Heat transfer

Heat flow throughout concrete is determined by applying the energy conservation requirement to Fourier's heat conduction law [17]:

$$\rho_c c_q \frac{\partial T}{\partial t} = \operatorname{div}\left(\lambda \overrightarrow{\nabla}(T)\right) \tag{23}$$

where ρ_c is the density of concrete, c_q is the concrete specific heat capacity, λ is the thermal conductivity of concrete and T is the temperature inside the concrete matrix at time t.

3. Numerical solution

In order to study the evolution of chloride ingress in concrete, it is necessary to simultaneously solve the system of PDEs represented by Equations 2, 13 and 23. The variation of C_{fc}, h and T throughout the considered mesh for a given time t is computed by using the finite element method. The evolution of spatial distribution is integrated in time by using the finite difference Crank-Nicolson method. To solve the system of PDEs, this work implements the methodology developed by Martín-Pérez et al. [10]. Such methodology uses linear triangular and rectangular elements and bilinear singly and doubly infinite elements to mesh the domain. The infinite elements are used to simulate the existence of material beyond the unexposed boundaries.

3.1. Boundary conditions

At the exposed boundaries, the conditions are defined as fluxes of chlorides, relative humidity or heat crossing the surface (Robin boundary condition). The chloride flux normal to the concrete surface, J_c^s, is:

$$J_c^s = \underbrace{B_c \left(C_{fc}^s - C_{env}\right)}_{\text{diffusion}} + \underbrace{C_{env}\, J_h^s}_{\text{convection}} \tag{24}$$

where B_c is the surface chloride transfer coefficient, C_{fc}^s is the concentration of free chlorides at the concrete surface, C_{env} is the concentration of chlorides in the surrounding environment and J_h^s is the humidity flux normal to the concrete surface which is defined by:

$$J_h^s = B_h \left(h^s - h_{env}\right) \tag{25}$$

where B_h is the surface humidity transfer coefficient, h^s is the pore relative humidity at the concrete surface and h_{env} is the relative humidity in the environment. For heat transfer, the boundary condition is given by the heat flux across the concrete surface, q^s:

$$q^s = B_T \left(T^s - T_{env}\right) \tag{26}$$

where B_T is the heat transfer coefficient, T^s is the temperature in the concrete surface and T_{env} is the temperature in the surrounding environment.

3.2. Solution procedure

Figure 1 depicts the algorithm used to determine the time-dependent variation of the profiles of temperature, humidity and chlorides for one dimension –e.g., x. For the first iteration ($i = 1$) the initial values of temperature, humidity and concentration of free chlorides can be supposed as constants for all points inside the mesh –e.g. T_{ini}, h_{ini} and $C_{fc,ini}$. Commonly the concentration of free chloride is set at zero at the beginning of the assessment. However, a given profile of chlorides can be used for existing structures. Thus, the algorithm to determine the profiles for a given time t_i is summarized in the following steps:

1. the actual temperature profile is determined from Equation 23 by considering the initial temperature profile $T(x; t = t_{i-1})$;
2. with the temperature profile estimated in the previous step $T(x; t = t_i)$ and the initial humidity profile $h(x; t = t_{i-1})$, the actual humidity profile is determined from Equation 13; and finally;
3. Equation 2 is solved by accounting for the actual profiles of temperature and humidity throughout the concrete and the initial values of free chlorides $C_{fc}(x; t = t_{i-1})$.

The procedure is repeated for the next i ($t_i = t_{i-1} + \Delta t$) by considering the previous profiles as initial values. The major difficulty in estimating the profiles of humidity and chlorides lies in the fact that Equations

2 and 13 are nonlinear because the diffusion coefficients and the isotherms depend on the actual profiles of humidity and chlorides; consequently, an iterative procedure is implemented. This procedure uses the profiles of h and C_{fc} obtained from the previous iteration, as the initial values and iterates until a given convergence criterion is reached. For example, for the profile of humidity in one dimension (i.e., x), the considered convergence criterion is:

$$\left| \frac{h(x;t_i)^{k+1} - h(x;t_i)^k}{h(x;t_i)^k} \right| \leq \varepsilon \tag{27}$$

where k represents the iterations to find $h(x;t_i)$, $h(x;t_i)^k$ is the humidity profile for the previous iteration, $h(x;t_i)^{k+1}$ is the humidity profile for the actual iteration and ε denotes a specified convergence parameter. A successive under-relaxation method is also implemented to increase the convergence rate. This method estimates a new humidity profile, $h^*(x;t_i)^{k+1}$, that is used as initial value for the next iteration:

$$h^*(x;t_i)^{k+1} = \omega h(x;t_i)^{k+1} + (1-\omega)h(x;t_i)^k \tag{28}$$

where ω is the relaxation factor varying between $[0-1]$.

3.3. Deterministic example

3.3.1. Problem description

The chloride penetration model allows introducing several mechanisms of ionic transfer in various environmental conditions. The assessment of chloride ingress by considering both unsaturated media and time-dependent variation of temperature, humidity and surface chloride concentration, is illustrated in this section. Before performing a stochastic modeling, a deterministic analysis is needed to confirm that the results are physically compatible with underlying mechanisms and to analyze the sensitivity of the model to environmental actions. Towards this aim, the evolution of environmental parameters is modeled by deterministic functions which can be considered as mean trends. Thus, the following assumptions are made:

- the flow of chlorides occurs in one-dimension (e.g., concrete slab);
- the structure is exposed to de-icing salts;
- the concrete is made with 400 kg/m^3 of Ordinary Portland Cement (OPC) with 8% of C_3A and water/cement ratio $w/c = 0.5$; and
- the concrete hydration time, t_e, is 28 days.

To account for seasonal variations of temperature and humidity, a sinusoidal variation is supposed:

$$T(t) = \frac{\phi_{max} + \phi_{min}}{2} + \frac{\phi_{max} - \phi_{min}}{2} \sin(2\pi t) \tag{29}$$

$$h(t) = \frac{\phi_{max} + \phi_{min}}{2} + \frac{\phi_{max} - \phi_{min}}{2} \sin(2\pi(t - 0.5)) \tag{30}$$

where $T(t)$ and $h(t)$ are the temperature or humidity at time t, ϕ_{max} is the maximum temperature or humidity, ϕ_{min} is the minimum temperature or humidity and t is expressed in years. There exists correlation between temperature and humidity. In this work, this correlation is taken into account by considering that the water-vapor required to saturate air during cooler seasons is lower, and therefore, relative humidity is larger for these seasons. On the contrary, relative humidity has lower values for warmer seasons. Figure 2a shows the temperature and humidity models used in this example. The values of temperature and humidity, ϕ, as well as the other constants used in the example are presented in Table 1.

In general, in chloride ingress modeling, it is assumed that the concentration of chlorides in the surrounding environment remains constant for the exposure to de-icing salts [29, 30]. However, since the kinematics of chloride ingress changes as function of weather conditions, a modified model for de-icing salts exposure is adopted in this work. This model considers that during the hot seasons the chloride concentration at the surface is zero, whereas during the cold seasons it becomes time-variant (Figure 2b):

$$C_{env}(t) = \begin{cases} 0 & \text{for } t < t_1 \\ C_{env}^{max}(t - t_1)/(t_2 - t_1) & \text{for } t_1 \leq t < t_2 \\ C_{env}^{max}\left[1 - (t - t_2)/(t_2 - t_1)\right] & \text{for } t_2 \leq t < t_3 \end{cases} \tag{31}$$

where C_{env}^{max} is the maximum chloride concentration that corresponds with the minimum temperature and returns to zero at the beginning of the hot season (see Figure 2b). It is worthy to clarify that the value of C_{env}^{max} has been defined by considering that the quantity of chloride ions deposited during one year be the same that the average annual concentration reported in the literature, C_{env}^{ave}. For this example the value of C_{env}^{max} presented in Table 1 entails that $C_{env}^{ave} = 4$ kg/m^3 [29, 30].

3.3.2. Influence of environmental variations on chloride penetration

Figure 3a depicts the profiles of chlorides for different seasons after one year of exposure. The analysis begins at the end of exposure to chlorides (middle of spring) and ends when $C_{env}(t)$ is maximum (middle of winter). It should be noted that although de-icing salts are not applied during spring, summer and fall, the penetration front advances towards the reinforcement. Chloride ingress is more appreciable from spring to summer than from summer to fall because chloride diffusivity increases for higher temperatures and humidities (see Equations 10 and 12). It can also be observed that during winter the chloride concentration tends to C_{env}^{max} at the exposed surface.

Given that the shape of the chloride profiles depends on the season, Figure 3b presents the profiles after 1, 5 and 25 years of exposure at the middle of spring. These profiles were calculated for two types of environmental actions: time-variant and time-invariant. For the former the temperature and humidity are estimated from Equations 29 and 30 and the surface chloride concentration form Equation 31. In the latter, all the environmental variables are considered as constants –i.e., $C_{env}^{ave} = 4$ kg/m^3, $T_{env} = 12.5$ °C and $h_{env} = 0.7$. For both cases, note that there is a large increase in the penetration depth from 1 to 5 years.

Nevertheless, the rate of chloride ingress decreases from 5 to 25 years. This reduction is due mainly to the decrease of chloride diffusivity with time –i.e., Equation 11. If the cover thickness, c_t, is 4 cm, it is also observed that for exposures higher than 5 yr the time-variant model gives greater concentration at c_t. This result is due to the acceleration of chloride penetration during hot and wet seasons. This analysis confirms that transfer mechanisms are very sensitive to environmental actions. Therefore, it is needed to model these actions as realistic as possible. Given that probabilistic methods can be used to take into account their randomness, the next section presents a stochastic approach to improve the previous representation.

3.3.3. Comparison with the analytical error-function solution

The most commonly used equation to model chloride penetration in concrete is the so-called "error-function solution" to Fick's second law [1]. However, this analytical solution is not valid neither for curve-fitting exposure data nor for predictions because the diffusivity and the surface chloride content are both time-dependent [31, 32]. Since this solution is still largely used, this section compares the results obtained with the proposed numerical approach with the results coming from the analytical error-function solution. To simplify the analysis, the inputs for temperature, humidity and surface chloride concentration are similar to those defined for the time-invariant case previously described (i.e., constant). Given that there is no experimental data to compute equivalent parameters for the analytical model, they have been computed from chloride profiles coming from the numerical model. The error function solution has two main governing parameters namely the surface chloride concentration and the chloride diffusion coefficient. Since the surface chloride concentration is supposed to be constant for both models –i.e., $C_{env}^{ave} = 4$ kg/m^3, the problem is reduced to estimate the chloride diffusion coefficient. This parameter is therefore found by minimizing the difference between the data coming from analytical and numerical solutions.

The analytical model uses a time-invariant chloride diffusion coefficient. Then, a chloride diffusion coefficient could be determined from each chloride profile. For instance, for the chloride profiles presented in Figure 3b and the time-invariant case, the chloride diffusion coefficients for the analytical model are: 1.46×10^{-12} m^2/s, 9.25×10^{-13} m^2/s and 6.26×10^{-13} m^2/s for 1, 5 and 25 years, respectively. It is noted that the instantaneous chloride diffusion coefficient is time-variant and decreases with time. This study compares the chloride profiles computed from the numerical and the analytical models. Two chloride diffusion coefficients were considered in the profiles coming from the analytical model. These diffusion coefficients were obtained from the numerical results at 1 and 25 years. Figure 4 presents the chloride profiles estimated in both cases. It is noted in Figure 4a that analytical and numerical results are closer for 1 yr. In the second case (Figure 4b), it is observed that the analytical solution tends to average the numerical solution for 25 years. However, the shape of the error-function solution is very different from the shape of the numerical solution. These differences emphasize the importance of including other phenomena in the calculation –i.e., chloride binding, a time-dependent chloride diffusion coefficient, etc. Besides, these results show that the

analytical solution is very sensitive to the data used to determine the chloride diffusion coefficient, and consequently, can over- or under-estimate the service life. Therefore, the lifetime assessment based on the error function solution of Fick's law should be used with care.

4. Probabilistic analysis of chloride penetration

There is significant uncertainty related to environmental conditions, material properties, cover and model parameters. Therefore, to give appropriate estimations of chloride ingress into concrete, the model described in section 2 is introduced into a stochastic framework. The probabilistic approach proposed in this paper does not include spatial modeling of the uncertainties. Although spatial variability has been recognized as an influencing issue for probabilistic lifetime assessment of corroding RC structures [33], this section focuses on the determination of time-invariant and time-variant probabilistic models for chloride ingress. Stewart and Suo [34] present a comprehensive methodology to take spatial modeling of the uncertainties into account.

4.1. Probability of corrosion initiation

The corrosion initiation time, t_{ini}, is defined as the instant at which the chloride concentration at the cover reaches a threshold value, C_{th}. This threshold concentration represents the chloride concentration for which the rust passive layer of steel is destroyed and the corrosion reaction begins. Note that this threshold is sensitive to the chemical characteristics of concrete components: sand, gravel, cement. Consequently, it is assumed in this paper that C_{th} is a random variable. Time to corrosion initiation is obtained by evaluating the time-dependent variation of the chloride concentration in the cover depth by using the solution of the PDEs presented in section 3. The cumulative distribution function (CDF) of time to corrosion initiation, $F_{t_{ini}}(t)$, is defined as:

$$F_{t_{ini}}(t) = P\{t_{ini} \leq t\} = \int_{t_{ini} \leq t} f(\underline{x})\, d\underline{x} \tag{32}$$

where $\underline{x}$ is the vector of the random variables to be taken into account and $f(\underline{x})$ is the joint probability density function of $\underline{x}$. The limit state function becomes:

$$g(\underline{x},t) = C_{th}(\underline{x}) - C_{tc}(\underline{x},t,c_t) \tag{33}$$

where $C_{tc}(\underline{x},t,c_t)$ is the total concentration of chlorides at the depth c_t and the time t and c_t is the thickness of the concrete cover. The failure probability, p_f, represents, in this case, the probability of corrosion initiation and is obtained by integrating the joint probability function on the failure domain:

$$p_f = \int_{g(\underline{x},t) \leq 0} f(\underline{x})\, d\underline{x} \tag{34}$$

Given the complexity of the solution procedure used to estimate the time-dependent evolution of chloride profiles (section 3), closed-form solutions for both the CDF of time to corrosion initiation and probability

of corrosion initiation are impossible. Therefore, an appropriate tool to deal with this kind of problem is to use Monte Carlo simulations. This study also implements Latin Hypercube sampling to reduce the computational cost of simulations. For the adopted probabilistic approach, the random variables are classified into two groups: *time-invariant* and *time-variant*. The first group of variables depends on both the material properties and the construction procedure. Therefore, it can be assumed that time-invariant random variables remain constant during one Monte Carlo simulation. The material properties, cover thickness, and model parameters are included among these variables. The second group encompasses random variables changing during the period of analysis. Relative humidity, temperature and chloride concentration in the surrounding environment are considered as time-variant random variables and are modeled by stochastic processes as described in the following sections.

4.2. Stochastic modeling of weather: humidity and temperature

In order to make a good estimation of the time to corrosion initiation, it is important to implement a model that realistically reproduces the temperature and the humidity during the period of analysis. In this context, stochastic processes were used to model the random nature of these weather parameters. According to Ghanem and Spanos [27], there are two rational methods to deal with the problem under the probabilistic scheme: Karhunen-Loève expansion or polynomial chaos. Taking into account the simplicity of the implementation and the computational time, Karhunen-Loève expansion is appropriate to represent the weather variables.

4.2.1. Karhunen-Loève expansion

Analogous to Fourier series, the Karhunen-Loève expansion represents a stochastic process as a combination of orthogonal functions on a bounded interval –i.e. $[-a, a]$. The development of a stochastic process by the Karhunen-Loève method is based on the spectral decomposition of the covariance function of the process $C(t_1, t_2)$. Since the covariance function is symmetric and positive definite, its eigenfunctions are orthogonal and form a complete set of deterministic orthogonal functions, $f_i(t)$, which are used to represent the stochastic process. The random coefficients of the process $\xi_i(\theta)$ can also be considered orthogonal or, in other words, statistically uncorrelated. Let $\kappa(t, \theta)$ be a random process, which is function of the time t defined over the domain $\mathbf{D}$, with θ belonging to the space of random events $\mathbf{\Omega}$, $\kappa(t, \theta)$ can thus be expanded as follows [27]:

$$\kappa(t, \theta) \simeq \bar{\kappa}(t) + \sum_{i=1}^{n_{KL}} \sqrt{\lambda_i} \xi_i(\theta) f_i(t) \tag{35}$$

where $\bar{\kappa}(t)$ is the mean of the process, $\xi_i(\theta)$ is a set of normal random variables, n_{KL} is the number of terms of the truncated discretization and λ_i are the eigenvalues of the covariance function $C(t_1, t_2)$ resulting from

the evaluation of the following expression:

$$\int_{\mathbf{D}} C(t_1, t_2) f_i(t_2) dt_2 = \lambda_i f_i(t_1) \tag{36}$$

The solution of Equation 36 can be analytically determined when the covariance function is exponential or triangular. In this work it is assumed that the processes of temperature and humidity have an exponential covariance of the form:

$$C(t_1, t_2) = e^{-|t_1 - t_2|/b} \tag{37}$$

where b is the correlation length and must be expressed in the same units of t. For this case, the expressions to compute $f_i(t)$ and λ_i are presented in detail in [27]. Finally, the mean of the stochastic process, $\bar{\kappa}(t)$, is modeled as a sinusoidal function which considers the effect of seasonal variations of the weather parameters –i.e., Equations 29 and 30. An advantage of this approach is that both the covariance function and the correlation length of weather parameters can be determined based on real measurements. Figure 5a shows some realizations of the stochastic process representing temperature where the parameters for the time-variant mean are described in Table 1. The considered correlation lengths are 0.1, 1 and 10 years; and the truncated discretization includes 30 terms ($n_{LK} = 30$). Note that for lower values of b the process is far from the mean and extreme values are frequently observed.

4.3. Stochastic modeling of surface chloride concentration

The model described in this subsection is used to represent the surface chloride concentration produced by de-icing salts application. Due to lack of data about the variation of C_{env} during the exposure time and that various studies indicate that C_{env} has a log-normal distribution [29, 30], the stochastic process representing C_{env} is generated with independent log-normal numbers (log-normal noise). The mean of C_{env} is described by Equation 31 and the COV used to generate the process is defined based on previous probabilistic studies [29, 30]. Stochastic representations of the surface chloride concentration are presented in Figure 5b. This figure considers a maximum surface chloride concentration, C_{env}^{max}, equal to 16 kg/m^3 and COVs of 0.2 and 0.4. As expected, the variability of the stochastic process increases for high values of COV.

5. Illustrative example

5.1. Problem description and basic assumptions

The main goal for this example is to study the influence of chloride binding, weather conditions, concrete aging, convection, correlation length and two-dimensional chloride ingress on the probability of corrosion initiation. Figure 6a shows the studied RC wall and column. It can be noted that chlorides come from one

direction for the one-dimensional exposure; whilst there is a source of chlorides in each side for the two-dimensional exposure. It is assumed herein that the structure is located well away from the seashore. Then, chlorides only come from de-icing salts. The weather features are presented in Table 1 and the probabilistic models used in this study are shown in Table 2.

The statistical parameters of the threshold concentration are defined based on the values reported in [30], where C_{th} is defined as the critical chloride content which leads to deterioration or damage of the concrete structure when the structure is constantly humid. The cover thickness, c_t, follows a truncated normal distribution with the statistical parameters indicated in Table 2 [29, 30]. The means of the reference diffusion coefficients of humidity and chlorides, $D_{h,ref}$ and $D_{c,ref}$, are assigned according to the experimental values presented in [3] for $w/c = 0.5$. The probabilistic models and COVs of $D_{h,ref}$ and $D_{c,ref}$, follow the distributions suggested in [9, 30]. Based on the sources presented in Table 1, it is supposed that α_0, n, U_c, λ and c_q follow beta distributions with the mean reported by the authors and varying between the limits established experimentally. The COVs of these variables were determined on the basis of the experimental results reported in Table 1. According to Val [22], the age reduction factor m also follows a beta distribution. Finally taking as a reference the typical density of normal concrete, it is assumed that this variable is normally distributed with a COV of 0.04 [35].

Other assumptions of this example are:

- the concentration of chlorides inside concrete is zero at the beginning of the analysis;
- the finite difference weighting factor is 0.8, and the relaxation factor is $\omega = 0.9$;
- the structure is located in a partially-saturated environment;
- the studied concrete contains 400 kg/m^3 of Ordinary Portland Cement (OPC) with 8% of C_3A and $w/c = 0.5$;
- the constants of the isotherms are $\alpha_L = 0.1185$, $\beta_L = 0.09$, $\alpha_F = 0.256$, $\beta_F = 0.397$ and were obtained for ordinary OPCs with the same characteristics [14, 15];
- the hydration period, t_e, is 28 days;
- the COV used to generate the stochastic process of C_{env} is equal to 0.4;
- the range of each random variable is divided into 10 equally probable intervals for the Latin Hypercube sampling and
- the random variables are independent.

5.2. Results

The results of Monte Carlo simulations were adjusted to an appropriate PDF, where the test of Kolmogorov-Smirnov (K-S) with a significance level of 5% was used as selection criterion. For all the studied cases, and according to [36], the results indicate that the time to corrosion initiation is log-normally distributed.

Figure 6b depicts the influence of the type of weather model –i.e., time-invariant, time-variant and stochastic, on the PDF of the corrosion initiation time. For the time-invariant case the annual temperature and relative humidity were set to 12.5°C and 0.7, respectively. Such values correspond to the annual mean for the time-variant model. The time-variant case accounts for the sinusoidal variation of temperature and humidity described by Equations 29 and 30 and the values presented in Table 1. The stochastic case considers the stochastic model presented in subsection 4.2 where the mean is defined by the time-variant model and the correlation length is 0.1 year. It should be noted that the mean and standard deviation of the corrosion initiation time decrease when both the seasonal variations and the randomness of humidity and temperature are considered. Taking as a reference the mean obtained from the stochastic analysis, it is observed that the mean of the corrosion initiation time is increased by 23% and 94% for the time-variant and time-invariant models, respectively. This increase is expected because as showed in Figure 3b, accounting for the seasonal variation of humidity and temperature (time-variant model) reduces the corrosion initiation time. The reduction is more appreciable when the time-variant model is coupled with a stochastic process, for which there are extreme values that accelerate chloride penetration. Give that under real exposure the structure is subject to random environmental actions, these results highlight the importance of including comprehensive probabilistic models of weather actions in the chloride ingress assessment.

The effect of chloride binding and the type of isotherm on the PDF of the corrosion initiation time is showed in Figure 7a. This analysis considers temperature and humidity as stochastic processes with a correlation length of 0.1 year. As expected, the results indicate that ignoring the effect of chloride binding reduces the mean of the corrosion initiation time in comparison to the cases where this effect was considered. This behavior seems reasonable because when binding is not considered, it is assumed that all the chlorides involved in the flow (bound and free) ingress simultaneously into the concrete matrix, and therefore, the time to corrosion initiation occurs early. By comparing the results for the Langmuir and Freundlich isotherms, it can be observed that there is no significant difference for both models. This similarity lies in the fact that the constants for both isotherms were determined for concrete with identical characteristics. It allows to suggest that for this type of studies, no improvement in this direction is needed.

The impact of convection on the PDF of the corrosion initiation time is plotted in Figure 7b. These PDFs were obtained for the Langmuir isotherm, correlation length of 0.1 year, and by modeling environmental actions stochastically. It can be noted from Figure 7b that accounting for chloride ingress by convection slightly decreases the mean of the corrosion initiation time. This reduction is due to the addition of a second mechanism of chloride ingress (i.e., convection) which augments the chloride concentration at the corrosion

cell reducing the time to achieve the threshold concentration. In this example, the effect of convection on chloride penetration is not very important because the structure is not subjected to cycles of wetting and drying. However, under other exposure conditions, wetting-drying cycles accelerate appreciably chloride penetration by carrying chloride ions with water.

Figure 8a describes the influence of the correlation length b (i.e., Equation 37) on the probability of corrosion initiation. For this study correlation lengths of 0.1, 0.5 and 1 year, have been simply assumed. Although this value should be determined based on real measurements of temperature and humidity for a determined place, the results indicated that its influence on the mean and standard deviation of the probability of corrosion initiation is not important. Moreover, it is noticed that the smaller values of b lead to conservative results. This behavior is expected because smaller values of b entail the presence of extreme values (see Figure 5a) that accelerate the process of chloride ingress.

Finally, the variation of the probability of corrosion initiation for 1-D and 2-D exposures is showed in Figure 8b. Both cases include the probabilistic nature of environmental actions, chloride ingress by convection, chloride binding and a correlation length of 0.1 years. As expected the higher probabilities correspond to the 2-D exposure. The reduction of the corrosion initiation time is due to the exposure to chlorides on both sides of the structural element. For instance, for 30 years of exposure the probability of corrosion initiation is increased by 27% when 2-D exposure is considered. These results stress the importance of including a two-dimensional analysis for correct prediction of corrosion initiation in small RC elements as columns and beams.

6. Conclusions and further work

This paper presented a stochastic approach to assess chloride ingress into concrete considering the effects of chloride binding, temperature, humidity, concrete aging and convection. The problems of chloride transport, moisture transport and heat transfer into concrete were treated by combining the finite element formulation with finite difference. The model of chloride penetration was introduced in a stochastic framework where Monte Carlo simulations and Latin hypercube sampling were used to account for the randomness related to the phenomena. The proposed probabilistic approach distinguishes between two types of random variables "time-invariant" and "time variant". The latter are treated as stochastic processes which are modeled by Karhunen-Loève expansions and log-normal noise.

The proposed approach is illustrated by a numerical example where the factors controlling the chloride ingress and the effect of weather conditions were studied. Overall behavior indicates that the mean of corrosion initiation time decreases when the randomness and seasonal variations of humidity, temperature and C_{env} and convection are considered; and increases when chloride binding is taken into account. By comparing chloride penetration in one- and two-dimensions, it has been found that high probabilities of

corrosion initiation correspond to the 2-D exposure. These results stress the importance of including the effects and the random nature of temperature, humidity, surface chloride concentration, chloride binding, convection and two-dimensional chloride ingress for a comprehensive lifetime assessment.

There are many areas in which further research is needed to improve the probabilistic model of chloride penetration. These improvements as summarized as follows:

- determination of model parameters for a wide range of concrete types;
- formulation and implementation of a model that considers the kinematics between concrete cracking and chloride penetration;
- study of the influence of hourly, daily and weekly variations of temperature and humidity on chloride ingress;
- assessment and consideration of the correlation of material properties and climatic conditions from experimental data;
- consideration of the spatial variability of the phenomenon; and
- characterization and modeling of error propagation in the whole deterioration process.

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Table 1: Values used in the deterministic example.

Chloride transport	**Moisture transport**	**Heat transfer**
$C_{env}^{max} = 16$ kg/m^3	$h_{min} = 0.6$	$T_{min} = -5$ °C
$D_{c,ref} = 3 \times 10^{-11}$ m^2/s [3]	$h_{max} = 0.8$	$T_{max} = 30$ °C
$\alpha_L = 0.1185$ [15]	$D_{h,ref} = 3 \times 10^{-10}$ m^2/s [9, 3]	$\lambda = 1.4$ W/(m °C) [25]
$\beta_L = 0.090$ [15]	$\alpha_0 = 0.05$ [16, 17]	$c_q = 1000$ J/(kg °C) [25]
$U_c = 41.8$ kJ/mol [21]	$n = 10$ [16, 17]	$B_T = 7.75$ W/(m^2 °C) [26]
$B_c = 1$ m/s [3]	$U = 25$ kJ/mol [3, 23]	
$m = 0.15$ [22]	$B_h = 3 \times 10^{-7}$ m/s [24]	

Table 2: Probabilistic models of the random variables.

Variable	**Mean**	**COV**	**Distribution**
C_{th}	0.5 wt% cement	0.20	normal
c_t	40 mm	0.25	normal (truncated at 10 mm)
$D_{h,ref}$	3×10^{-10} m^2/s	0.20	log-normal
α_0	0.05	0.20	beta over [0.025;0.1]
n	11	0.10	beta over [6;16]
$D_{c,ref}$	3×10^{-11} m^2/s	0.20	log-normal
m	0.15	0.30	beta over [0;1]
U_c	41.8 kJ/mol	0.10	beta over [32;44.6]
ρ_c	2400 kg/m^3	0.04	normal
λ	2.5 W/(m ^{o}C)	0.20	beta over [1.4;3.6]
c_q	1000 J/(kg ^{o}C)	0.10	beta over [840;1170]

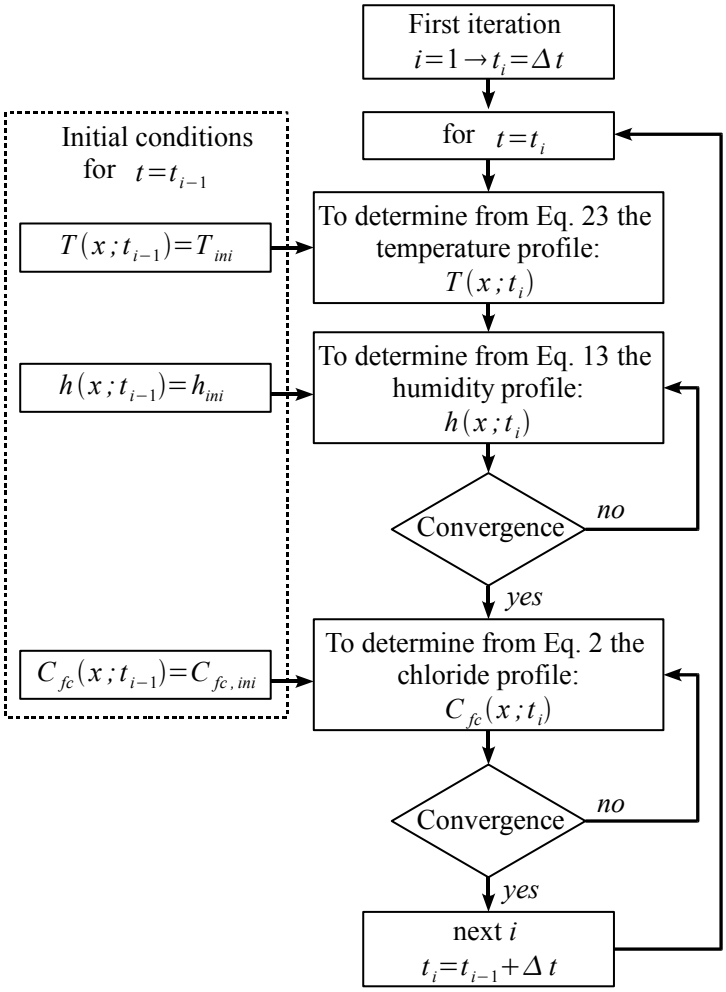

Figure 1: Algorithm for estimating the profiles of temperature, humidity and chlorides.

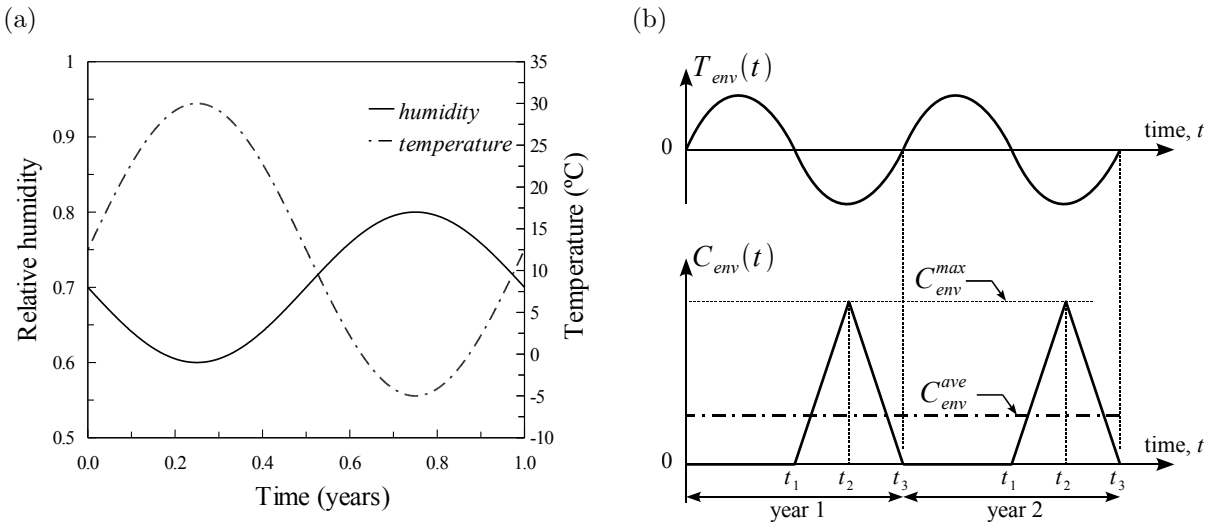

Figure 2: (a) Temperature and humidity models. (b) Environmental chloride surface concentration.

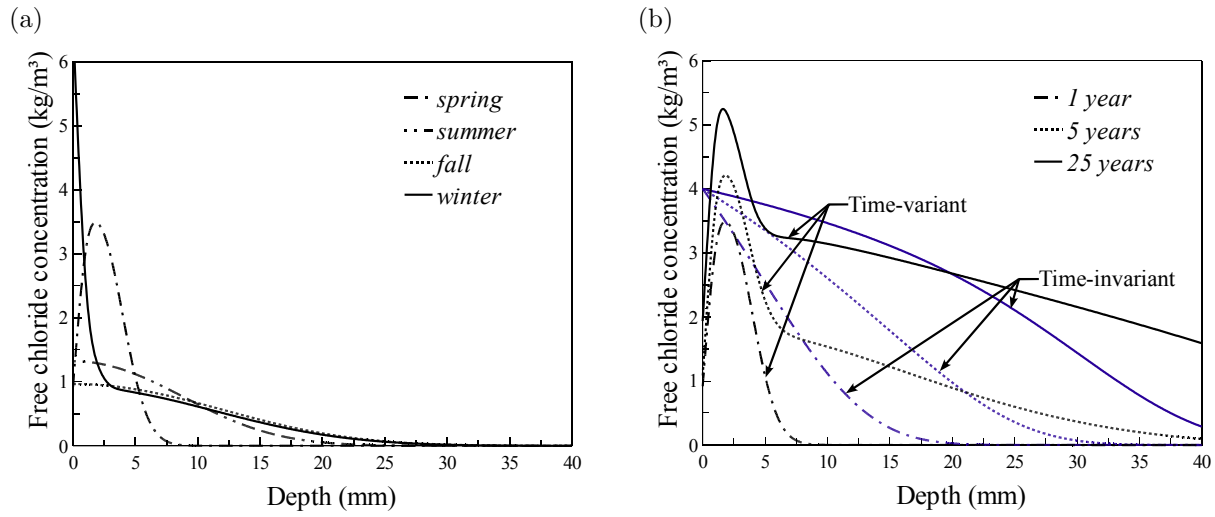

Figure 3: Profiles of C_{fc} for (a) different seasons after one year of exposure and (b) the middle of spring and various times of exposure.

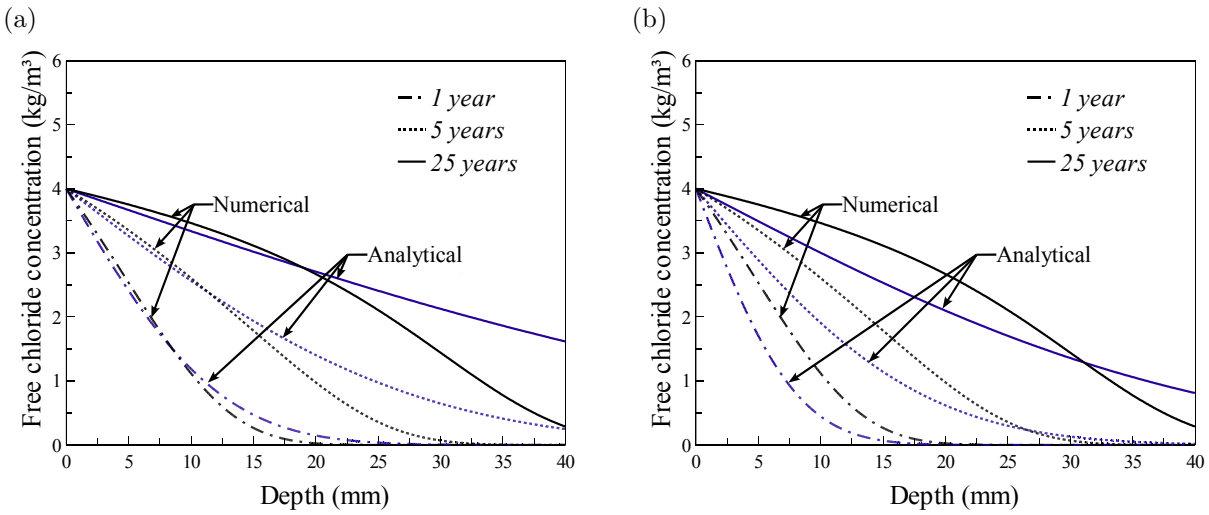

Figure 4: Chloride profiles for the analytical model and the numerical solution for diffusion coefficients estimated at (a) 1 year and (b) 25 years.

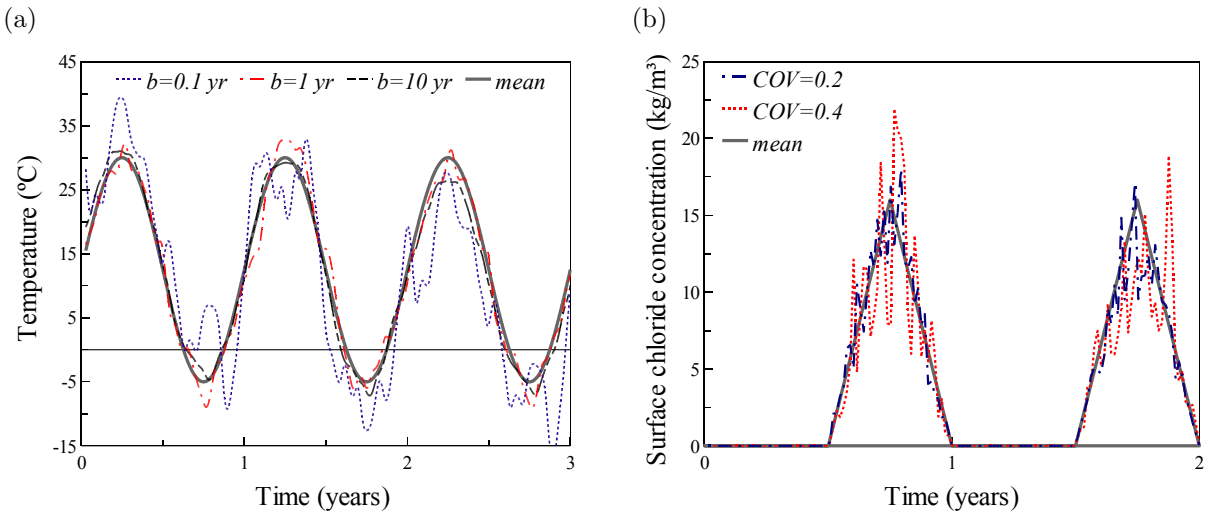

Figure 5: Realizations of (a) temperature and (b) surface chloride concentration.

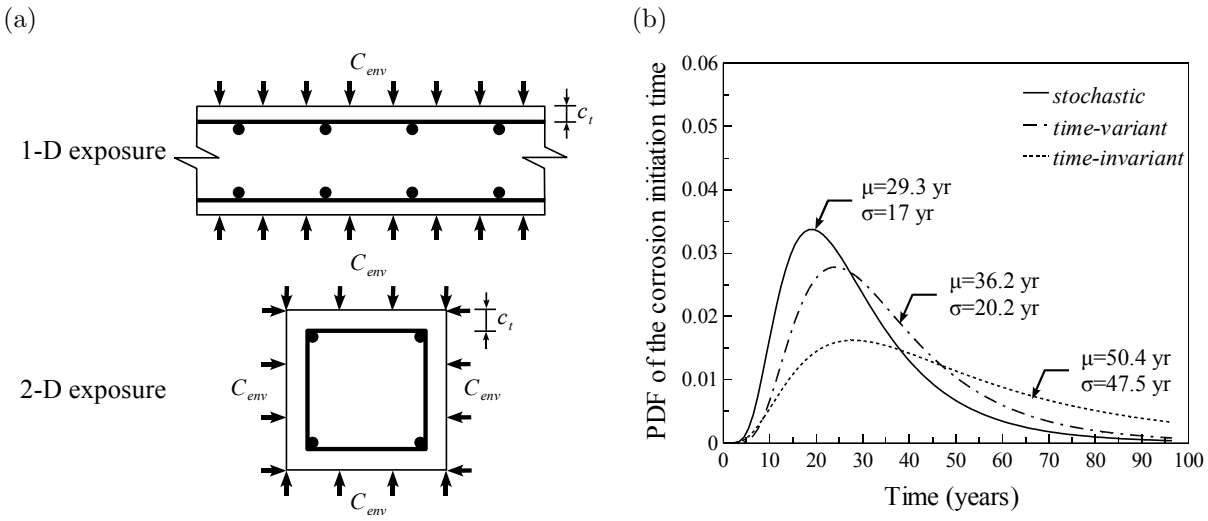

Figure 6: (a) Cross-sections of the studied RC wall and column. (b) Impact of weather model.

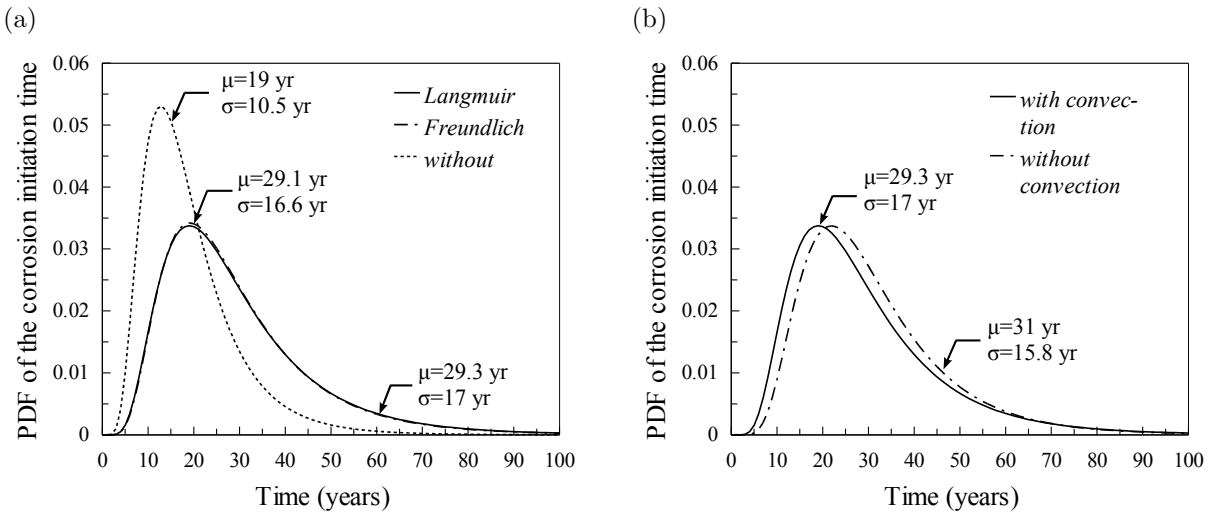

Figure 7: Effect of (a) binding and type of isotherm and (b) convection.

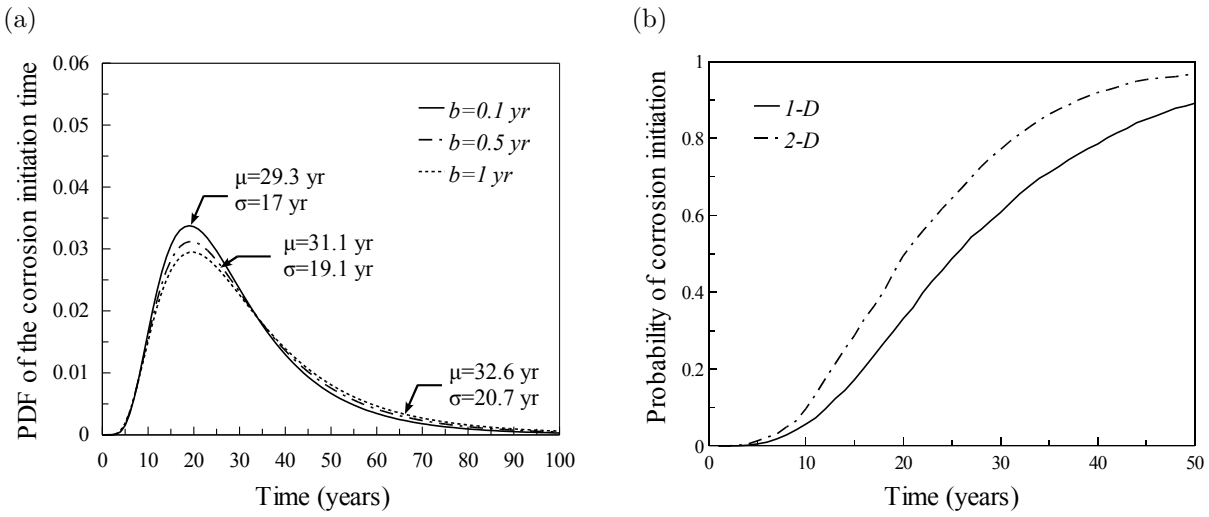

Figure 8: (a) Influence of the correlation length b. (b) Probability of corrosion initiation for 1-D and 2-D exposures.